



## Enhanced removal of methyl violet using NaOH-modified *C. camphora* leaves powder and its renewable adsorption

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### ABSTRACT

In this study, the enhanced removal of cationic dye, methyl violet (MV), from aqueous solution with NaOH-modified *C. camphora* leaves powder (N-CLP), compared with *C. camphora* leaves powder (CLP), was demonstrated. Subsequently, the effects of solution pH, initial MV concentration, contact time, and temperature on the adsorption of MV by N-CLP were systematically studied. The experimental results showed that MV adsorption on N-CLP was pH-dependent and stable adsorption could be achieved at pH 4.0–10.0. Electrostatic adsorption and  $\pi$ - $\pi$  stacking could be involved in adsorption. The adsorption process for MV on N-CLP followed pseudo-second-order kinetics model. Equilibrium adsorption data were well fitted to the Langmuir isotherm model. The adsorption process is endothermic, spontaneous and random. The adsorption property of second-regenerated N-CLP and third-regenerated N-CLP still had 0.85 times over that of N-CLP and the N-CLP could be used as a renewable bio-adsorbent for removal the refractory pollutants in wastewater.

**Keywords:** NaOH-modified *C. camphora* leaves powder; Adsorption; Adsorbent; Methyl violet

### 1. Introduction

Removal of dyes from wastewater is essential due to extreme toxicity of dyes towards aquatic life and humans. Nowadays, there are more than 10,000 dyes commercially available [1]. These dyes are widely used in textile, paper dyeing industries, rubber, plastics, cosmetics, laboratory experiments, etc. Meanwhile, almost 1,000 tones dyes flowed into streams as wastewater worldwide every year [2]. The dyes in dyeing wastewater discharged directly from factories seriously impair the growth of organisms, and even endanger the safety of humans [3,4].

To address aforementioned concerns, various methods and techniques have been developed for removal of dyes in wastewaters [5–8]. Among these methods, adsorption in which various adsorbents are employed for the removal of dyes, is the most promising approach to offer the best prospects because of its simple operation, high performance and

low cost [9]. Owing to its high adsorption capacity, activated carbon is the most commonly used adsorbent for removal of refractory organics in wastewaters. However, the wide application of activated carbon in wastewater treatment is limited due to its high cost [10,11]. Therefore, renewable, simply prepared, cost-effective bio-sorbents from natural materials, such as plum kernels [12], sawdust [13], coconut bunch waste [14], bagasse fly ash [15], peat [16–18], chitin [19], chitosan [20], perlite [21], wood [22], banana pith [23–25], coir pith [26,27], orange peel [28], were successfully used for the removal of dyes from aqueous solution, and have been considered as alternatively low-cost adsorbents for removal of dyes in wastewater.

*C. camphora* tree, a broad-leaved subtropical plant that mainly stands in northern latitudes 10 to 30° and distributes in roadside, parks and schools in south of China, is one of these natural materials that could provide leaves as bio-sorbents for the treatment of wastewater. Except for use for extracting essential oil [29], Chen et al. used *C. camphora* leaves to adsorb Pb(II) [30] and copper(II) [31]. Pre-

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vious work done in our group [32] demonstrated that the  $q_e$  reached 74.9 mg g<sup>-1</sup> and the removal percentage reached 90% at initial MV concentration of 50 mg L<sup>-1</sup> and adsorbent dosage of 0.6 g L<sup>-1</sup>, when *C. camphora* were used to adsorb MV in aqueous solution. To further increase the adsorption capacity of the adsorbent from agricultural and forestry residues, various modifying methods have been developed, for which the Langmuir isotherm is widely used to indicate the modifying effectiveness. These modifying methods could be roughly categorized into two groups, physical and chemical modifying methods. However, the chemical modifying methods are the most promising approaches because of its high modifying effectiveness. For chemical modifying methods, a wide variety of chemical modifying agents can be employed, e.g. HCl, H<sub>3</sub>PO<sub>4</sub>, KOH, NaOH, Fe(NO<sub>3</sub>)<sub>3</sub> and NaHCO<sub>3</sub>, but the most common used chemical modifying agents are alkaline chemical modifying agents, such as KOH, NaOH, and NaHCO<sub>3</sub>. Shao et al. [33] reported that NaOH-modified cornstalks enhanced the  $q_e$  for lead (II). Guo et al. [34] reported that KOH-modified maize straw enhanced the  $q_e$  for cadmium(II). Cara et al. [35] reported that NaHCO<sub>3</sub>-modified straw enhanced the adsorption of residual Metribuzin in the soil. Ren et al. [36] reported that NaOH-modified phoenix tree leaves enhanced adsorbing crystal violet. However, to the best of our knowledge, there is still no report about modified *C. camphora* leaves and the modifying effect on adsorption property of *C. camphora* leaves. Hence, in this work, the *C. camphora* leaves powder was modified in NaOH solution, and the adsorption experiment, adsorption process theory, proposed adsorption mechanism, desorption-readsorption of NaOH-modified *C. camphora* leaves were investigated.

## 2. Experimental sections

### 2.1. Preparation of adsorbent and reagents

The *C. camphora* leaves collected in the campus of Xiangtan University were washed repeatedly with deionized water for several times until the dirty particles and soluble impurities were completely removed. The washed leaves were dried for 24 h in a drying oven at 333 K. Then, the crisp leaves were crushed into powder in a crushing mill and then sieved. The obtained powders with particle size in the range of 100–300 mm were called as *C. camphora* leaves powder (CLP). Subsequently, the CLP was modified by being impregnated in 0.1 mol L<sup>-1</sup> NaOH solution with a ratio of 1:25 (g CLP: mL NaOH) for 48 h, then the NaOH-impregnated CLP were washed with deionized water repeatedly until the pH of the filtrate is neutral. The dried NaOH-modified CLP was abbreviated as N-CLP and sealed in glass bottle for further adsorption experiments. Hydrochloric acid (37%, wt.%), sodium hydroxide (analytical reagent, AR), potassium nitrate (AR), MV (AR) were purchased from Tianjin Kermel Chemical Reagent Company limited and used as received. Deionized water was used in all experiments.

### 2.2. SEM image

The surface structure of N-CLP was visualized and analyzed by SEM (Zeiss, Supra TM 55 microscope).

### 2.3. FT-IR characterization

FT-IR (Spectrometer 2000 FT-IR) from 4000 cm to 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> was carried out to characterize the N-CLP and CLP.

### 2.4. pH<sub>zpc</sub> measure of N-CLP

The zero point of charge (pH<sub>zpc</sub>) of N-CLP was determined by referring to literatures [32,37]. A batch of 100 mL flasks were filled with 50 mL of 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> solutions at different initial pH (pH<sub>i</sub>) values in the range of 2–12, and 0.05 g N-CLP was charged in these flasks, respectively. Then, the suspensions were sealed and shaken for 24 h with shaking speed of 130 rpm at room temperature in a constant temperature shaker. The final pH (pH<sub>f</sub>) values of the supernatant liquid were noted. The difference ( $\Delta\text{pH} = \text{pH}_i - \text{pH}_f$ ) between the initial pH value and final pH values was plotted against the pH<sub>i</sub>. The point of intersection of the resulting curve with abscissa gave the pH<sub>zpc</sub>.

### 2.5. Adsorption experiments

#### 2.5.1. Batch adsorption experiments

The effect of pH, adsorbent dose, contact time and temperature on the adsorption for MV on the N-CLP were investigated by batch adsorption experiments. Batch adsorption experiments were performed in a 250 mL stoppered flasks by contacting a definite mass of N-CLP with 50 mL of MV solution at a certain pH (the pH was adjusted with 0.1 mol L<sup>-1</sup> NaOH and HCl aqueous solution). The mixture of N-CLP and MV solution was shaken in a constant temperature shaker at shaking speed of 130 rpm until adsorption equilibrium. 5 mL of mixture at adsorption equilibrium was taken out and centrifuged at 4000 rpm for 2 min. The residual MV concentration in the supernatant was analyzed using a spectrophotometer (UV-2450) at 586 nm wavelength. The amount of MV adsorbed per unit mass of adsorbent at equilibrium, named as adsorption capacity at equilibrium  $q_e$  (mg g<sup>-1</sup>), was estimated from Eq. (1), the removal percentage (R%) of the MV on adsorbent was calculated from Eq. (2).

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

$$R\% = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

where  $C_0$  and  $C_e$  (mg g<sup>-1</sup>) are the concentrations of MV at initial and equilibrium, respectively;  $V$  (L) is the volume of MV solution; and  $M$  (g) is the mass of N-CLP used.

#### 2.5.2. Effect of contact time and adsorption kinetic experiments

The adsorption kinetic experiments were carried out as described in literature [32]. The detailed experimental step as follows: 0.2 g N-CLP and 500 mL of MV solution at initial concentration of 30, 50, and 70 mg L<sup>-1</sup> were charged in a 1000 mL of glass beakers. And the glass beakers was

on a mechanical stirrer at rotate speed of 120 rpm at room temperature. At time zero and pre-defined time intervals, 1 mL of the dye solutions were taken from the beaker and the residual MV concentration was determined. The amount of MV adsorbed per unit mass of the N-CLP ( $q_t$ , mg g<sup>-1</sup>) at different times ( $t$ ) was calculated from Eq. (3).

$$q_t = \frac{(C_0 - C_t) \times V}{M} \quad (3)$$

where  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) is the concentrations of MV at initial and  $t$ , respectively;  $V$  (L) is the volume of MV solution; and  $M$  (g) is the weight of N-CLP used.

### 2.5.3. Desorption and recycling adsorption

The mixture of 0.08 g of N-CLP and 200 mL of MV solutions at initial concentration of 50 mg L<sup>-1</sup> was shaken for 12 h at room temperature. The adsorbents loaded MV were separated and soaked in 1 mol L<sup>-1</sup> of HCl solution repeatedly till the HCl solution was colorless, and then the desorbed adsorbent was washed by deionized water till the filtrate was neutral. The collected desorbed N-CLP was abbreviated as regenerated N-CLP and reused for dye removal after drying. The cycles of adsorption–desorption processes were successively conducted 4 times.

## 3. Theory of adsorption process

### 3.1. Adsorption kinetic studies

The pseudo-first-order (PFO), pseudo-second-order (PSO) kinetic and intra-particle diffusion models were employed to study the adsorption kinetic of MV by N-CLP. The PFO and PSO model can be expressed as the following Eqs. (4) and (5) [38,39], respectively. The intra-particle diffusion equation is expressed as the following Eq. (6)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_p \sqrt{t} + c \quad (6)$$

where  $k_1$  (min<sup>-1</sup>) is PFO adsorption rate constant;  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is PSO adsorption rate constant;  $k_p$  is the particle diffusion rate constant (mg g<sup>-1</sup> min<sup>-0.5</sup>),  $c$  is the intercept (mg g<sup>-1</sup>).

### 3.2. Adsorption isotherms studies

In this work, Langmuir [Eq. (7)] and Freundlich [Eq. (8)] isotherm models were employed to fit the adsorption equilibrium data of MV on N-CLP.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m} \times \frac{1}{C_e} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where  $q_m$  (mg g<sup>-1</sup>) is the maximum adsorption amount of the monomolecular layer,  $b$  (L mg<sup>-1</sup>) is the Langmuir constant related to adsorption energy,  $K_F$  is the Freundlich isotherm constant,  $n$  is a dimensionless constant known as heterogeneity factor.

### 3.3. Thermodynamic parameters studies

Thermodynamic parameters including Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be calculated according to the following equations:

$$K_L = \frac{q_e}{C_e} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_L \quad (10)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where  $K_L$  is distribution coefficient,  $T$  is absolute temperature whose units are K and  $R$  is gas constant ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

## 4. Results and discussion

### 4.1. SEM image of N-CLP

The surface morphology of N-CLP was observed through SEM shown in Fig. 1. It is obvious that the N-CLP surface is rougher and alveolate. Meanwhile, some porous structures are clearly observable on the surface of N-CLP, implying an increase exposure of number of active adsorption sites and an improvement in the adsorption efficiency.

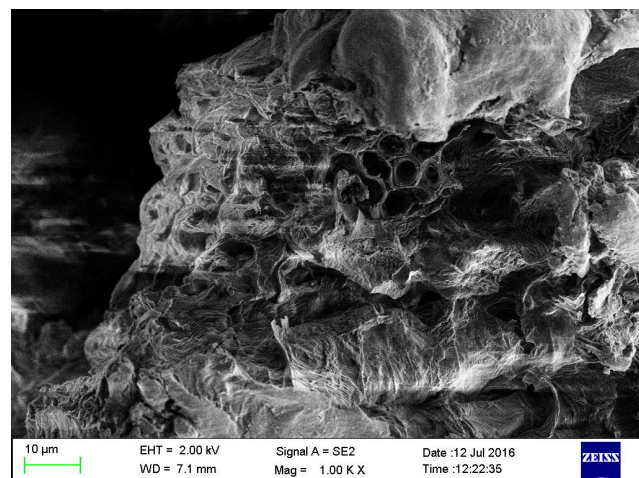


Fig. 1. SEM image of N-CLP.

#### 4.2. Comparing adsorption experiment of N-CLP and CLP

Comparison adsorption experiment of MV by N-CLP and CLP was conducted by adding 0.02 g CLP or N-CLP in 50 mL MV solution at initial concentrations of 30, 50, 70, 90, 110 mg L<sup>-1</sup>, respectively. The results are shown in Fig. 2, the adsorption property of N-CLP is stronger than that of CLP. The increase range of adsorption capacity and removal percentage is more obvious in higher initial concentration solution. The results suggested that the adsorption property of CLP enhanced after being modified by NaOH. Similar results were reported by Shao et al. [33] investigating the effect of the modifying of cornstalks with NaOH on the  $q_e$  for lead (II). The improved adsorption effect is ascribed to functional groups such as hydroxyl groups, which were exposed or get modified after being treated with NaOH and get involved in the process of adsorption.

Fig. 3 illustrates the FT-IR spectra of CLP and N-CLP. As shown in Fig. 3, the signal of broad peak at 3314 cm<sup>-1</sup> for stretch vibration of –OH in N-CLP is stronger than that in CLP. In addition, –OH group inclines to bind cationic ion. This may be responsible for the stronger adsorption property of N-CLP to MV, compared to CLP.

#### 4.3. Factors on adsorption for MV on N-CLP

##### 4.3.1. Effect of pH

The pH value in the dye solution affects not only the surface charge of adsorbents, but also the dissociation of adsorbates [40]. Most of the dye molecules exist in ionic form in the solution, and the solubility depends on the degree of dissociation. So, the adsorption level is significantly affected by the pH value in the solution. MV is a triphenylmethane cationic dye, and its precipitation will accelerate due to the limited solubility of MV at pH > 10.0 [41,42]. Hence, the influence of pH on the adsorption for MV on N-CLP was carried out at pH 2.0–10.0. As shown in Fig. 4, the  $q_e$  sharply increased at pH 2–4, subsequently, the  $q_e$  remained at pH 4–10. The results are due to the surface potential of N-CLP which is associated with the pH value in the solution and the  $pH_{pzc}$  of N-CLP

(the inset in Fig. 4 illustrated the  $pH_{pzc}$  of N-CLP). Moreover, the results depended on the dissociation degree of MV. MV is readily to be adsorbed through  $\pi$ – $\pi$  stacking and ionic interaction because it is an alkaline and cationic triphenylmethanedyne [41]. At pH <  $pH_{pzc}$ , the N-CLP surface associates with H<sup>+</sup> ions and becomes positively charged. The positively charged N-CLP repels positively charged MV. Hence, the adsorption for MV on N-CLP could occur primarily through the  $\pi$ – $\pi$  stacking which results in a lower  $q_e$ . As pH value of solution increases, the negative charges on N-CLP surface increases, the repellent gradually weakens, and, finally, the electrostatic attraction between negatively charged N-CLP and positively charged MV and the  $\pi$ – $\pi$  stacking enhance the  $q_e$ . Zhao et al. [43] reported similar results in the investigation of the effect of pH on the adsorption of naphthalene and 1-naphthol on sulfonated graphene. Li et al. [41] also reported similar results in the investigation of the effect of pH on the adsorption of MV on modified nano-graphite/Fe<sub>3</sub>O<sub>4</sub> composite. The proposed simple adsorption mechanism for MV on N-CLP at different pH is illustrated in Fig. 5.

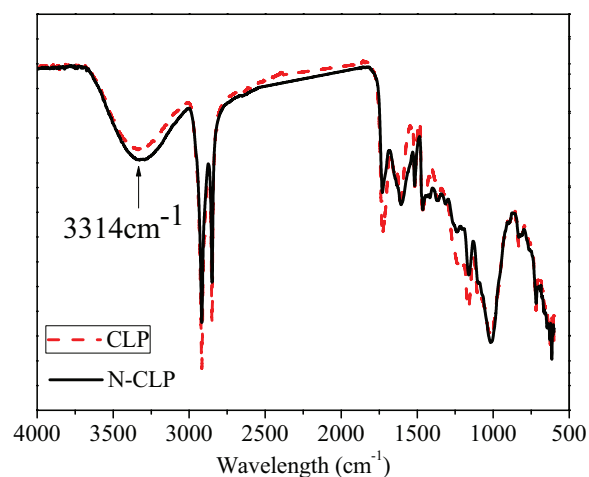


Fig. 3. FT-IR spectrum of CLP and N-CLP.

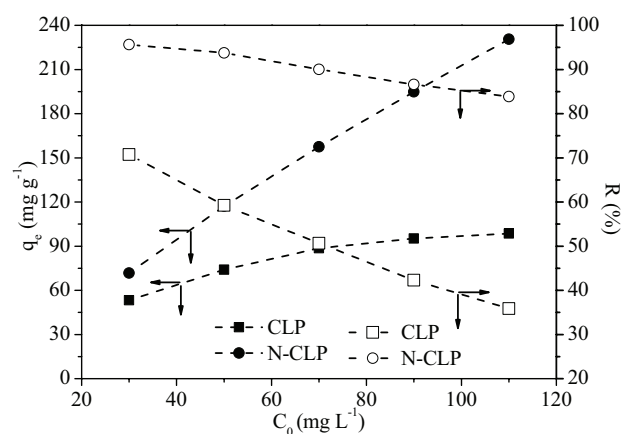


Fig. 2. The  $q_e$  and  $R$  (%) of N-CLP (NaOH-modified) and CLP (N-CLP and CLP dosage: 0.4 g L<sup>-1</sup>, pH: nature pH of MV solution, at room temperature).

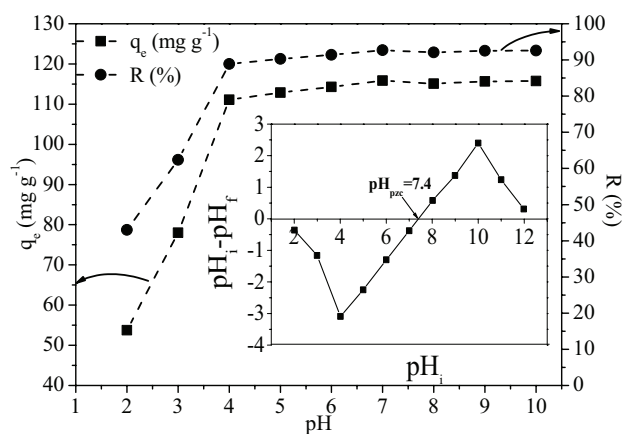


Fig. 4. Effect of pH on the adsorption for MV on N-CLP (N-CLP dosage: 0.4 g L<sup>-1</sup>, initial MV concentration: 50 mg L<sup>-1</sup>, at room temperature).

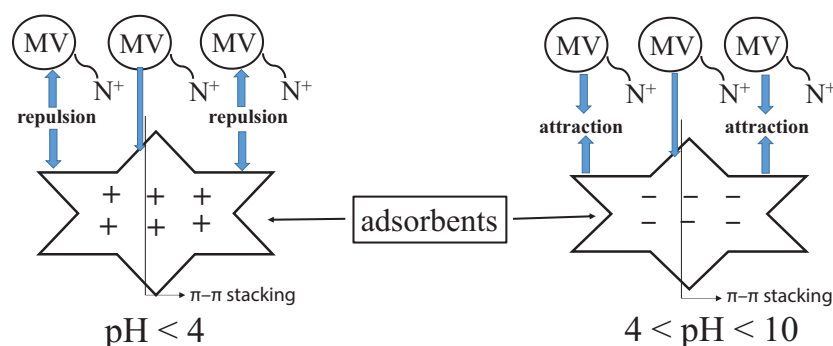


Fig. 5. Proposed adsorption mechanism for MV on N-CLP.

#### 4.3.2. Effect of dosage on the adsorption for MV on N-CLP

The effect of the adsorbent dosage on the adsorption for MV on N-CLP was investigated at N-CLP dosage of 0.2, 0.4, 0.6 g L<sup>-1</sup>. The results are shown in Fig. 6. As shown in Fig. 6, the  $q_e$  increased with increasing initial MV concentration and with decreasing N-CLP dosage, as well as the increased removal percentage with increasing N-CLP dosage and decreasing initial MV concentration. This results could be ascribed to the large number of available adsorption sites at higher adsorbent dosage or in lower MV concentration solution. Moreover, the removal percentage at dosage of 0.4 g L<sup>-1</sup> was closed to that at dosage of 0.6 g L<sup>-1</sup> in the initial MV concentration range studied here. At dosage of 0.4 g L<sup>-1</sup>, the removal percentage was over 95% at initial MV concentration of 10, 30 mg L<sup>-1</sup>, the removal percentage reached 85% even if the initial concentration was at 90 mg L<sup>-1</sup>. So, dosage of 0.4 g L<sup>-1</sup> was selected in the other adsorption experiments in this work.

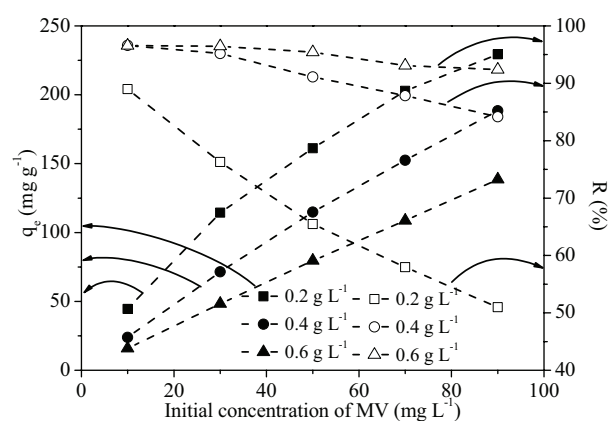


Fig. 6. Effect of adsorbent dosage on adsorption for MV on N-CLP. (pH: nature pH of MV solution, room temperature).

#### 4.3.3. Effect of contact time on the adsorption for MV on N-CLP and kinetics modelling

The contact time ( $t$ ) of adsorbent and dye is very important because the adsorption rate constants can be calculated by fitting plots of  $q_t$  against  $t$ . In addition, the adsorption kinetics can be studied and the most suitable kinetics model could be proposed based on plot fittings. The results about the effect of contact time on the adsorption for MV on N-CLP are shown in Fig. 7. The results indicate that MV adsorption took place via three stages. Firstly, a fast adsorption that occurred within 90 min, followed by a slow phase of MV removal that developed from 90th min to 420th min. The third stage after 420th was an adsorption equilibrium or quasi-stabilised state. Moreover, quicker adsorption equilibrium in lower initial MV concentrations solutions and slower adsorption equilibrium in higher initial MV concentrations were observed.

The uptake of MV by N-CLP was modelled by employing PFO, PSO kinetics and intra-particle diffusion kinetics models which have been presented previously. Fig. 8(a–b) illustrate the linear fitting curve of plots of  $\ln(q_e - q_t)$  vs.  $t$  and  $t/q_t$  against  $t$ , respectively. Constants calculated from the slopes and intercepts of the linear fitting curve in Fig. 8a–b and the correlation coefficient ( $R^2$ ) are presented in Table 1. Compared to the lower  $R^2$  (0.965, 0.950, 0.419) of linear fit-

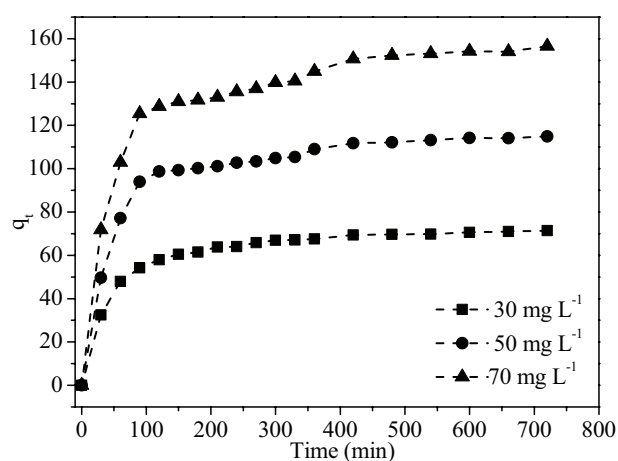


Fig. 7.  $q_t$  for MV on N-CLP as function of contact time (N-CLP dosage: 0.4 g L<sup>-1</sup>, pH: nature pH of MV solution, room temperature).

ting curve in Fig. 8a, the higher  $R^2$  (0.999, 0.999, 0.997) of linear fitting curve in Fig. 8b suggests that the PSO kinetic model is more suitable than PFO kinetic model to describe the MV uptake process by N-CLP. Moreover, the calculated  $q_{e2,cal}$  (73.9, 113.0, 161.6 mg g<sup>-1</sup>) from PSO model is closer to

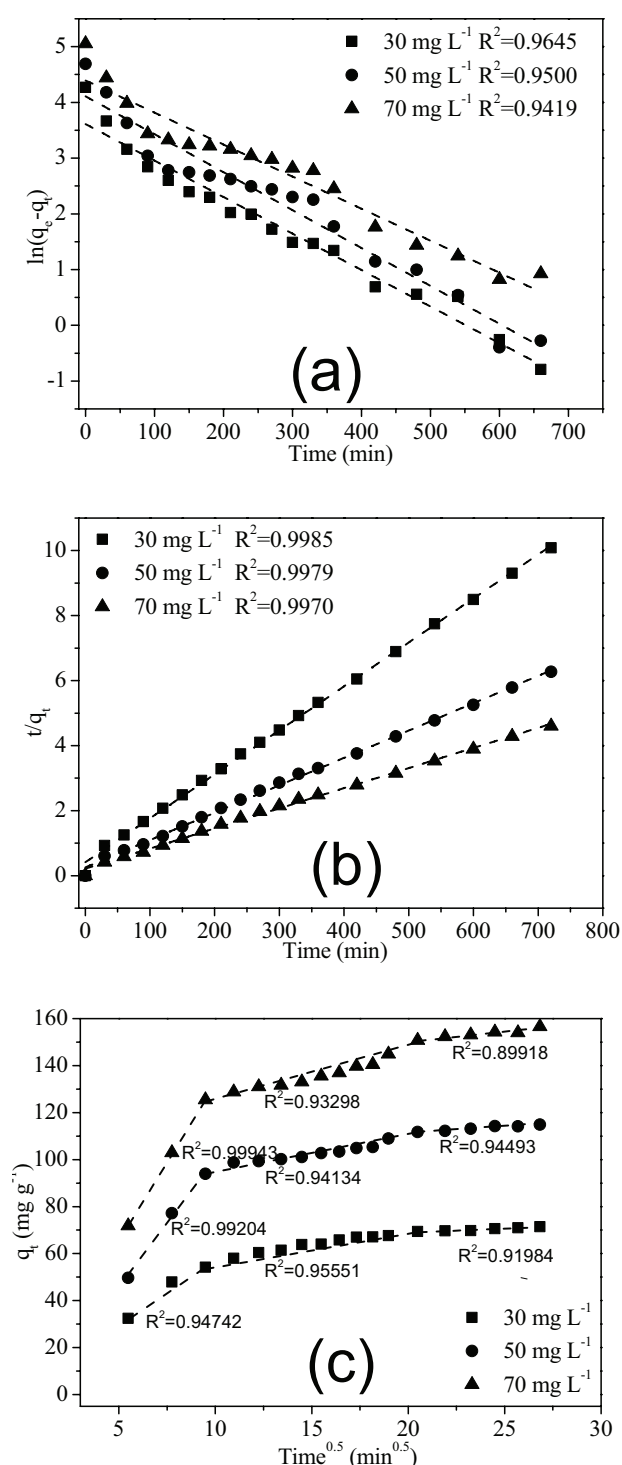


Fig. 8. Pseudo-first-order kinetic (a) pseudo-second-order kinetic (b) and intra-particle diffusion kinetic (c) modelling for MV adsorption on N-CLP.

experimental  $q_{e,exp}$  (71.4, 114.9, 156.5 mg g<sup>-1</sup>) than  $q_{e1,cal}$  (36.9, 60.8, 80.9 mg g<sup>-1</sup>) calculated from PFO kinetic model. These results further indicate that PSO model is more suitable than PFO kinetic model to describe the MV uptake process by N-CLP.

In order to study the diffusion mechanism, intra-particle diffusion kinetic model was employed to analyze the entire adsorption process and controlled rate step for MV uptake by N-CLP. Fig. 8(c) illustrates that, by plotting  $q_t$  against  $t^{0.5}$ , the lines did not cross the origin, and there are multi-linear regions in the intra-particle diffusion plots. The results suggest that internal diffusion is not the only rate-limiting step in the adsorption process, and three factors, including external surface adsorption, intra-particle diffusion stage and adsorption equilibrium, may be all involved to influence the adsorption process [44,45].

#### 4.3.4. Effect of temperature on the adsorption for MV on N-CLP and adsorption isotherm

The effect of temperature on the adsorption for MV on N-CLP was carried out at 10, 30, 50°C. As shown in Fig. 9, the increase  $q_e$  from 10°C to 30°C was more obvious than that from 30°C to 50°C, especially at higher MV initial concentration. Moreover, in practical wastewater treatment, it is not advised to carry out the adsorption experiment at 50°C due to the energy cost. Hence, in this work, the adsorption experiment was conducted at 30°C or room temperature.

The adsorption isotherms at 10, 30, 50°C were studied in this section. Fig. 10a–b illustrate the Langmuir and Freundlich adsorption isotherm for MV on N-CLP at 10, 30, 50°C. The linear fitting of Langmuir and Freundlich isotherm at different temperature was conducted. The  $q_m$  calculated from the intercept of plot by plotting  $1/q_e$  against  $1/C_e$  were 156.7, 206.6, 335.6 mg g<sup>-1</sup>, respectively. The  $q_m$  (206.6 mg g<sup>-1</sup>) of N-CLP at 30°C was much higher than that (104.2 mg g<sup>-1</sup>) of CLP that was not modified in NaOH solution [32]. The results indicate that the adsorption property of N-CLP increased sharply comparing to that of CLP. Moreover, for Langmuir isotherm, the  $R^2$  are 0.999, 0.999, 0.998, respectively, and much higher than the  $R^2$  (0.955, 0.975, 0.937) from Freundlich isotherm. The results suggest that Langmuir isotherm model fits the experimental data well and MV assumes a monolayer and homogenous adsorption on the N-CLP.

#### 4.3.5. Thermodynamic parameters

To further understand the feasibility and spontaneous nature of the adsorption process for MV on N-CLP, thermodynamic parameters, including Gibbs free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ), were studied. The  $\Delta G^0$  calculated from Eqs. (10), (11) is presented in Table 2. The values of  $\Delta H^0$  and  $\Delta S^0$  calculated from the slopes and intercepts of plots by plotting  $\ln K_L$  versus  $1/T$  are also presented in Table 2. The negative  $\Delta G^0$  indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [41,46,47]. Moreover, the decrease of  $\Delta G$  values with increasing temperature indicates the adsorption is more spontaneous at higher temperature, and confirms that N-CLP is more conducive to adsorb MV at higher temperature [48]. The positive  $\Delta H^0$  values implies that the adsorption process for MV on N-CLP was endothermic [41,47]. The positive  $\Delta S^0$  values suggest better attraction of MV toward N-CLP as well as increased randomness at the solid-solution interface during adsorption process [44].

Table 1

Adsorption rate constants,  $R^2$ ,  $q_e$  of pseudo-first-order kinetics and pseudo-second-order kinetics models for MV on N-CLP

| $C_0$ (mg L <sup>-1</sup> ) | Pseudo-first-order kinetic model |       |                                    | Pseudo-second-order kinetic model |       |                                    | $q_{e,exp}$ (mg g <sup>-1</sup> ) |
|-----------------------------|----------------------------------|-------|------------------------------------|-----------------------------------|-------|------------------------------------|-----------------------------------|
|                             | $k_1$ (min <sup>-1</sup> )       | $R^2$ | $q_{e1,cal}$ (mg g <sup>-1</sup> ) | $k_2$ (g(mg min) <sup>-1</sup> )  | $R^2$ | $q_{e2,cal}$ (mg g <sup>-1</sup> ) |                                   |
| 30                          | $1.51 \times 10^{-2}$            | 0.964 | 36.9                               | $0.044 \times 10^{-2}$            | 0.998 | 73.9                               | 71.4                              |
| 50                          | $1.57 \times 10^{-2}$            | 0.949 | 60.8                               | $0.027 \times 10^{-2}$            | 0.997 | 113.0                              | 114.9                             |
| 70                          | $1.32 \times 10^{-2}$            | 0.942 | 80.9                               | $0.018 \times 10^{-2}$            | 0.996 | 161.6                              | 156.5                             |

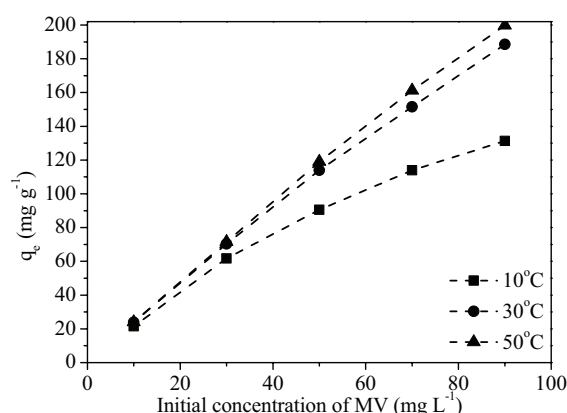
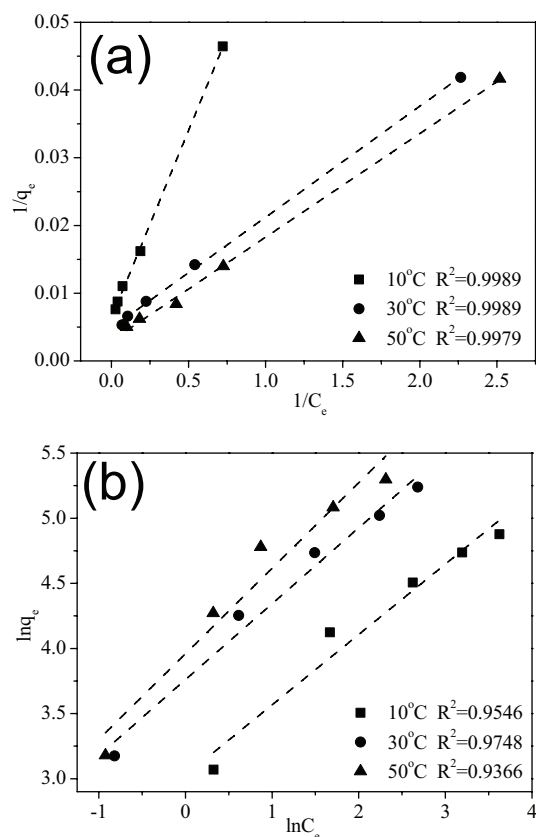
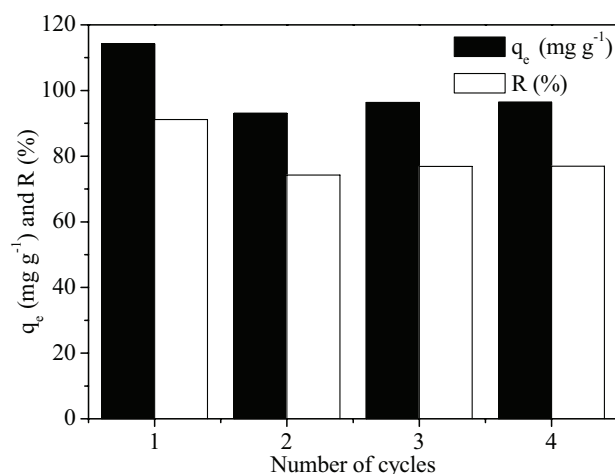
Fig. 9. Effect on temperature on the adsorption for MV on N-CLP (N-CLP dosage: 0.4 g L<sup>-1</sup>, initial MV concentration: 50 mg L<sup>-1</sup>, pH: nature pH of MV solution).

Fig. 10. Langmuir (a) and Freundlich (b) isotherm linear fitting for MV adsorption by N-CLP.

Table 2

Adsorption thermodynamic parameters for MV on N-CLP

| $C_0$ (mg L <sup>-1</sup> ) | $\Delta G$ (KJ mol <sup>-1</sup> ) at temperature (K) |         |         | $\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> ) | $\Delta H$ (KJ mol <sup>-1</sup> ) |
|-----------------------------|-------------------------------------------------------|---------|---------|---------------------------------------------------|------------------------------------|
|                             | 283.5                                                 | 303.5   | 323.5   |                                                   |                                    |
| 10                          | -6.468                                                | -10.072 | -11.032 | 117.019                                           | 26.324                             |
| 30                          | -5.789                                                | -8.204  | -10.622 | 120.844                                           | 28.473                             |
| 50                          | -4.437                                                | -6.333  | -10.079 | 139.027                                           | 35.246                             |
| 70                          | -3.633                                                | -5.946  | -7.443  | 96.126                                            | 23.502                             |
| 90                          | -2.953                                                | -5.707  | -6.729  | 96.293                                            | 24.094                             |

Fig. 11. The  $q_e$  and  $R$  (%) (removal percentage) of MV adsorption by N-CLP and regenerated N-CLP.

## 5. Desorption–re-adsorption studies

Reuse of the adsorbent is necessary for disposal of the loaded sorbent [49]. Hydrochloric acid is a better reagent for desorption [50]. 1 mol L<sup>-1</sup> of hydrochloric acid was used in this adsorbent regeneration experiments. Fig. 11 illustrates the  $q_e$  and the removal percentage for MV on the N-CLP and regenerated N-CLP. As shown in Fig. 11, compared to the  $q_e$  and removal percentage of MV by N-CLP, the  $q_e$  and removal percentage of MV by regenerated N-CLP decreased. At same adsorbent dosage and initial MV concentration, compared to the N-CLP, the  $q_e$  decreased from 114 mg/g to 93 mg/g and the removal percentage decreased from 91% to 74% for MV on first-regenerated N-CLP. The adsorption efficiency decreased for 18.5%. However, compared to first-regener-

ated N-CLP, the adsorption efficiency of second-regenerated N-CLP and third-regenerated N-CLP did not decrease, but increased slightly (about 3.3%) due to the modified function of hydrochloric acid [51]. In other words, compared to N-CLP, the adsorption efficiency of second and third-regenerated N-CLP decreased only 15%. The results suggest that N-CLP could be reused to adsorb pollutants.

## 6. Conclusions

An efficient and low-cost renewable adsorbent (N-CLP) was prepared by modifying the CLP with NaOH. Compared to  $q_e$  of MV by CLP, the  $q_e$  of MV by N-CLP enhanced. The stable adsorption of MV on N-CLP could be achieved at pH 4–10. Electrostatic adsorption and  $\pi$ - $\pi$  stacking could be involved in adsorption. Intra-particle diffusion is not the only rate-controlling step in the entire adsorption process. PSO kinetic model is suitable to describe the adsorption process. Langmuir adsorption isotherm models is suitable to fit the adsorption equilibrium data and MV assumes a monolayer and homogenous adsorption on the N-CLP. The adsorption of MV on the N-CLP is endothermic, random and spontaneous. The adsorption property of regenerated N-CLP still had 0.85 times over that of N-CLP. Hence, the N-CLP can be used as renewable adsorbent for removal of cationic dyes from wastewaters.

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